Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part XX. Fission-product Tellurium Off-gas Disposal in the Fluid-bed Fluoride Volatility Process

by

D. R. Vissers and M. J. Steindler

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Chemical Engineering Division

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ABSTRACT

The volatile fluoride species of fission-product tel-
lurium, tellurium hexafluoride, represents a troublesome
component in the fluid-bed fluoride-volatility process off-
gas system. The problem results from the relatively high
concentration of the highly toxic radioactive tellurium found
in spent reactor fuels and the chemically inert character of
tellurium hexafluoride found in the process off-gas system.

Gas sorption with tellurium hexafluoride on various
sorbents was studied, both in static and flowing type systems,
to evaluate 13 sorbents as potential trapping agents for tel-
lurium hexafluoride. Radio-tagged tellurium hexafluoride
was used in the gas-flow studies. These studies revealed
that activated alumina can effectively remove tellurium hexa-
fluoride from an off-gas stream containing fluorine. Tellu-
rium hexafluoride removal efficiencies in excess of 99.995%
were easily obtained. The heat of sorption for TeF_6 on acti-
vated alumina was found to be 4.8 kcal mole^{-1}. The TeF_6
sorptive ability of activated charcoal was also investigated.

I. INTRODUCTION

Fluid-bed fluoride-volatility processes are being developed for
treating spent power-reactor fuel. The volatile fluoride species of fission-
product tellurium represents a potentially troublesome component in the
process off-gas of these fluoride-volatility processes because of the
relatively high concentration of radioactive tellurium in the spent reactor
fuel[1,2] and the chemically inert character of tellurium hexafluoride formed
in the process. The low maximum permissible concentration for a 168-hr
week[3] (MPC_{168}) for continuous, occupational exposure to the insoluble form
of fission-product tellurium, ^{127m}Te, and ^{129m}Te of 1×10^{-8} Ci/m^3 adds to
the seriousness of the off-gas decontamination problem. Tellurium hexa-
fluoride has a biological half-life of 22 days,[4] which places it as an insoluble
form of tellurium.

The purpose of this investigation was to define the tellurium problem and to obtain information on means of removing tellurium from the off-gas stream of a fluid-bed fluoride-volatility process (FBFVP). The subject was first examined by reviewing the available related published and unpublished literature.[5] A conceptual fluid-bed fluoride-volatility processing plant was then devised in order to examine the problems relating to tellurium, and to estimate a decontamination factor for tellurium from the process off-gas. (These calculations are presented in Appendix B.)

This report describes the results of (1) a series of batch-type gas-solid sorption screening studies to identify the more promising reagents for removing tellurium hexafluoride, and (2) a series of dynamic gas-flow soprtion studies in which packed beds of the more promising reagents were evaluated quantitatively as sorbents for tellurium hexafluoride, using radiotagged tellurium. Heat-of-sorption studies were carried out with TeF_6 on activated alumina.

II. EQUIPMENT AND PROCEDURE

A. Reagents

The nonradioactive tellurium hexafluoride used in this study was obtained from the Allied Chemical Company and was purified by fractional sublimation under vacuum to remove the lower fluorides and oxyfluorides of tellurium, such as Te_2F_{10}, TeF_4, and $Te_3F_{14}O_2$. The molecular weight of the purified material was determined to be 243 g mole^{-1} (calculated, 241.6 g mole^{-1}), which was within the experimental error of the procedure used. Infrared studies of the purified product confirmed earlier spectra of TeF_6 (shown in Table I).

Radioactively tagged, powdered tellurium metal was obtained by chemically processing ^{125}Sb in the presence of carrier tellurium.[7] The tagged-tellurium metal powder was then fluorinated to the hexafluoride.[8] The reaction product was then purified, as described above. A vapor-pressure determination of the purified material agreed with the published values for TeF_6.[5]

TABLE I. Infrared Spectra of Tellurium Hexafluoride

This Work ν (obs) (cm^{-1})	Gaunt[6] ν (obs) (cm^{-1})	ν (calc)[6] (cm^{-1})	Assignment[6]
437	439	439	$ν_3 - ν_5$
511	509	510	$ν_5 + ν_6$
522	517	-	-
755	752	-	$ν_3$
872	871	871	$ν_2 + ν_6$
1425	1425	1426	$ν_2 + ν_3$
1453	1451	1453	$ν_1 + ν_3$

The fluorine used in the gas-flow sorption studies was obtained from an Air Products fluorine calibration standard cylinder. The solid reagents evaluated as sorbents in this study are listed in Table II. The surface area of these reagents was determined by standard B.E.T. techniques, assuming that a nitrogen molecule occupies 16.28 $\overset{\circ}{A}{}^2$ of surface area.

TABLE II. Reagents Evaluated for TeF_6 Removal

Material	Source	Designation	Surface Area[a] (m^2/g)
Activated alumina	Alcoa	F-1, -8 +14 mesh	295
BPL activated charcoal	Pittsburgh Coke and Chemical Company	-12 +30 mesh, BPL	2075
Activated cocoanut charcoal	Sargents	AC-11368	1790
Linde Molecular Sieve	Union Carbide Corporation	1/16 in., Type 13X	280
Linde Molecular Sieve	Union Carbide Corporation	1/16 in., Type 10X	332
Magnesium fluoride	Prepared at Oak Ridge National Laboratory	14-18 mesh	146
Sodium fluoride	Harshaw Chemical Company	1/8 x 1/8-in. tablets	<1
Soda lime	Mallinckrodt Chemical Works	4-8 mesh	6.3
Copper-metal turnings	Mallinckrodt Chemical Works	Reagent	<0.1
Nickel-metal wool	Brillo Manufacturing Company	Coarse grade	<0.1
Tellurium-metal powder	Sargents	Reagent	<1
Aluminum-metal turnings	ANL	2S, clean	<0.1
Copper(II) oxide	Allied Chemical	Reagent wire	<0.1

[a]Measured by B.E.T. method using nitrogen.

B. Experimental Equipment

1. Batch-type Sorption Equipment

The apparatus consisted of a general-purpose manifold, to which were attached a 97-ml vertical, tubular heated nickel reactor, a system of cold traps, a calibrated TeF_6 feed supply, a vacuum system, and a Booth-Cromer type pressure transmitter with a mercury-manometer readout.[9] The manifold, valves, reaction vessel, and all auxiliary equipment exposed to the tellurium hexafluoride were constructed of nickel. A Chromel-Alumel thermocouple within the nickel reactor served as the temperature indicator and regulator signal for the furnace temperature controller.

2. Gas-flow-type Sorption Equipment

The experimental apparatus consisted of (1) two packed beds of activated alumina in series, (2) a reagent supply, (3) radioactivity detection equipment, and (4) back-up traps. The TeF_6 flowrates were regulated with calibrated gas-bubblers charged with fluorolube. The air and fluorine gas flows were regulated with glass and Kel-F rotameters, respectively, The packed-bed reactors were constructed from 3/4-in.-diam, 1/32-in.-wall, 24-in.-long aluminum tubing, fitted in the center with a nickel screen, which served as a bed support. A plug of nickel wool above the bed held the solid charge in place. A tube furnace regulated by a thermocouple-controller system was used to heat the beds. The counting equipment consisted of two scintillation detectors, two single-channel analyzers, two count-rate meters, a scaler, and a dual-pen chart recorder. Packed beds of activated alumina and BPL activated charcoal served as the back-up traps for the system. Figure 1 is schematic diagram of the apparatus.
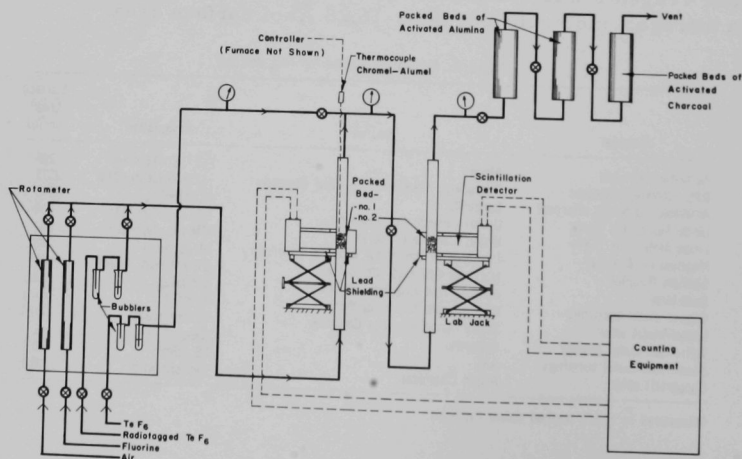
Fig. 1. Apparatus for Gas-flow Sorption Studies with T

3. Heat-of-sorption Equipment

The heat-of-sorption equipment was composed of the batch-type sorption equipment to which had been added an aqueous constant-temperature bath, equipped with a mercury-type thermoregulator.

C. Experimental Procedure

1. Batch-type Sorption Studies

A weighed sample of the sorbent was placed in the reactor and, after the system was evacuated and heated to the desired temperature, a measured quantity of tellurium hexafluoride was admitted to the system. The sorption of tellurium hexafluoride was monitored by observing the change of pressure in the system. After sorption was completed, the excess tellurium hexafluoride was collected in a cold trap cooled with liquid nitrogen. The vessel containing the sorbent was then evacuated, at approximately 10^{-2} Torr, through a second cold trap cooled by liquid nitrogen, to determine whether the tellurium hexafluoride could be desorbed from the solid. In some of the experiments, a second reactor vessel heated to 100°C and containing about 10 g of sodium fluoride pellets was placed in series with the principal reactor to collect any hydrogen fluoride that may have been present.

For each study, the initial TeF_6 pressure given is the pressure of the TeF_6 at 25°C. The characteristics of the Booth-Cromer and mercury-manometer readout limited the accuracy of the pressure measurement (± 0.3 mm). Consequently, the maximum sorption could not be reported as 100%.

2. Gas-flow-type Sorption Studies

The experimental procedure used in these studies consisted of passing radioactively tagged tellurium hexafluoride mixed with dry air, or with dry air and fluorine, at a fixed tellurium hexafluoride concentration and specific activity through the first packed bed of sorbent. The gas mixture leaving the top of the first bed was mixed with a suitable quantity of inactive TeF_6 to re-establish the initial TeF_6 concentration in the gas fed to the second bed of the same sorbent. The mixture was then fed into the bottom of the second bed. The packed beds each contained the same quantity of reagent. After a given quantity of TeF_6 had been passed through the beds, the TeF_6 gas flows were turned off, and the beds were purged with dry air for about 30 min. The quantity of ^{125m}Te sorbed on the respective beds was then determined in situ, using suitable counting equipment, to evaluate the ability of the particular packed bed to remove and retain TeF_6 from an air-TeF_6 or an air-TeF_6-F_2 gas mixture.

Counting efficiencies of two scintillation crystals for ^{125m}Te were evaluated with a ^{125m}Te standard. The apparent specific activity of the TeF$_6$ tagged with ^{125m}Te was evaluated by sorbing and counting a known quantity of the tagged TeF$_6$ on the sorbents in situ.

The isotopic dilution technique used in these studies is not new, but its use in gas-solid reaction systems has been limited. The primary advantage of the technique is that a complete analysis of the sorbent may be carried out at a fixed sorption species concentration, thus eliminating errors that result from variations in the concentration of TeF$_6$. The isotopic dilution technique permits ready evaluation of the decontamination factor (DF) across the packed beds, where DF is defined as the ratio of the tellurium hexafluoride concentration entering the bed to that leaving the bed. The ratio of the ^{125m}Te activity sorbed on bed number 1 to that sorbed on bed number 2 is equal to the DF across the first bed, given the following definitions and assumptions.

a. Definitions of Terms

A_1 = ^{125m}Te activity entering bed number 1.

A_2 = ^{125m}Te activity entering bed number 2, equal to the ^{125m}Te activity leaving bed number 1.

A_3 = ^{125m}Te activity leaving bed number 2.

A_{B_1} = ^{125m}Te activity sorbed on bed number 1.

A_{B_2} = ^{125m}Te activity sorbed on bed number 2.

b. Subscripts

B_1 = bed number 1.

B_2 = bed number 2.

c. Assumptions

$$DF_1 = DF_2$$

$$DF_1 = \frac{A_1}{A_2} \text{ (definition)}$$

$$DF_2 = \frac{A_2}{A_3} = DF_1$$

$$A_{B_1} = A_1 - A_2, \qquad A_{B_2} = A_2 - A_3$$

$$\frac{A_{B_1}}{A_{B_2}} = \frac{A_1 - A_2}{A_2 - A_3} = \frac{\frac{A_1}{A_2} - 1}{1 - \frac{A_3}{A_2}} = \frac{DF_1 - 1}{1 - \frac{1}{DF}} = DF \cdot \frac{DF - 1}{DF - 1} = DF.$$

The in situ counting of the columns also enables one to study the TeF_6 concentration gradient across the columns, and to determine whether the columns lose activity (i.e., TeF_6) during air purging or air-fluorine purging. The TeF_6 concentration gradient along the length of the column was determined by lowering the scintillation crystal 1/4 in. at a time; each crystal position was then counted, and a profile of the bed was obtained.

3.   Heat-of-sorption Studies

A weighed sample of activated alumina was placed in the reactor. The alumina was then evacuated and heated to about 200°C to remove sorbed gases. The system was then brought to the desired temperature, and a known amount of tellurium hexafluoride was introduced. Knowledge of the system volume and pressure allowed the weight of TeF_6 sorbed by the activated alumina to be calculated for any resultant pressure. A sorption blank with TeF_6 was obtained for the reactor system to correct for any surface sorption of TeF_6 on the surfaces of the equipment at the particular temperature.

III. EXPERIMENTAL RESULTS

A. Batch-type Sorption Studies

The capacity of most gas sorbents is principally determined by surface area, pore-size distribution, and the chemistry and geometry of the sorbent surface and sorbing gas molecule. The sorbents evaluated in this study were: activated alumina, activated charcoals, Linde Molecular Sieves, sodium fluoride, magnesium fluoride, soda lime, copper-metal turnings, nickel-metal wool, tellurium-metal powder, aluminum-metal turnings, and copper(II) oxide.

For comparative evaluation of the respective sorbents, the TeF_6 was assumed to be sorbed as a monolayer on the surface of the sorbent. The amount of tellurium hexafluoride sorbed, therefore, is expressed as percent loading, where the percent loading is based on the assumption that each sorbed TeF_6 molecule occupies 40 $\mathring{A}^2$ of nitrogen B.E.T. surface area on the sorbent at complete monolayer coverage. Thus, a square meter of B.E.T. sorbent surface area at 100% surface loading has a capacity of 4.15×10^{-6} mole of TeF_6. One gram of any material with a B.E.T. surface area of 1000 m^2/g would thus have a capacity of 1 g of TeF_6 at 100% loading.

1. Activated Alumina

Figure 2 shows a typical gas-sorption isotherm at 25°C for the sorption of TeF_6 on activated alumina. The isotherm indicates that about 50% of the TeF_6 present was sorbed in 30 sec, whereas only 76% of the TeF_6 was sorbed in 20 min. These results indicate that the rate of TeF_6 sorption on activated alumina is high until about 16% of the B.E.T. surface is covered. Several tests were performed in which the ratio of activated

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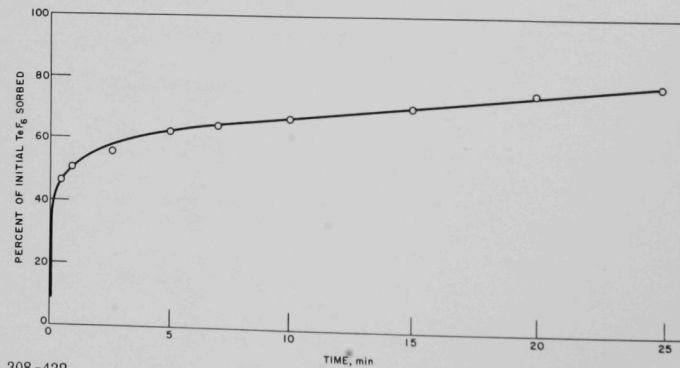
Fig. 2. Rate of Sorption of TeF_6 on Activated Alumina at 25°C. TeF_6 charge, 4×10^{-3} mole; initial pressure, 100 Torr; activated alumina charge, 10 g (TeF_6 monolayer capacity, 1.2×10^{-3} mole/g).

alumina to TeF_6 was increased so that if the entire quantity of TeF_6 were sorbed, it would occupy only 7.6% of the nitrogen-determined surface area of the activated alumina. The results of these tests indicate that the rate of TeF_6 sorption is high at low surface coverage. The studies with the higher ratio of activated alumina to TeF_6 were then extended to higher temperatures. The results of experiments with activated alumina (shown in Table III) indicate that below 300°C activated alumina is a good sorbent for TeF_6. After sorption of TeF_6 on activated alumina, nitrogen B.E.T. surface-area measurements of the samples were made (the results of which are shown in Table IV). Results indicate that only at 500°C does the activated alumina lose a significant fraction of surface area. Desorption of TeF_6 at 10^{-2} Torr was slight (as shown in Table III), indicating that TeF_6 is retained strongly by activated alumina.

TABLE III. Sorption Rate and Retention of Tellurium Hexafluoride on Activated Alumina

TeF_6 charge, 2×10^{-3} mole; initial pressure, 200 Torr;
activated alumina charge,[a] 22.2 g

Reaction Time (min)	Percent of the Initial TeF_6 Sorbed on Activated Alumina					
	25°C	100°C	200°C	300°C	400°C	500°C
0.5	>97	>99	99	>97	62	37
1.0	>98	>99	>99	>98	66	41
2.0	>98	>99	>99	>98	69	45
5.0	>99	>99	>99	>98	76	50
10.0	>99	>99	>99	>98	85	58
15.0	>99	>99	>99	>98	85	56
20.0	>99	>99	>99	>98	86	56

Temperature of Sorption and Desorption (°C)	Percent of Initial TeF_6 Desorbed from Alumina during Evacuation[b]
25	6.5
100	2
200	1.4
300	1.8
400	1.5

[a]The calculated TeF_6 monolayer capacity of the activated alumina was 1.2×10^{-3} mole/g.
[b]The alumina samples were placed under vacuum ($\sim 10^{-2}$ Torr) for desorption for 1-2 hr.

TABLE IV. B.E.T. Surface-area Measurements of Activated Alumina Samples

Reaction time: 20 min

Description of Activated Alumina	B.E.T. Surface Area (m^2/g)	Percent of Surface Covered with TeF_6
Material as received	295	-
Reacted at 100°C with TeF_6	297	7.4
Reacted at 200°C with TeF_6	316	7.5
Reacted at 300°C with TeF_6	303	7.4
Reacted at 400°C with TeF_6	316	6.4
Reacted at 500°C with TeF_6	155	~4

2. Activated Charcoal

a. <u>BPL Activated Charcoal</u>. The effects of loading of the charcoal surface by TeF_6 on (1) the kinetics of TeF_6 sorption and (2) the retention of TeF_6 by charcoal were investigated at 25°C. Table V presents the results of this study. To determine the effect of temperature on the TeF_6 sorption behavior, sorption studies were carried out at 100, 200, 300, and 400°C. The results, reported in Table VI, indicate that at 25°C charcoal possesses good sorptive characteristics for TeF_6 until about 16% of the B.E.T. surface area is covered by the sorbed TeF_6.

b. <u>Activated Cocoanut Charcoal</u>. To determine how the type of charcoal affects the sorptive properties of the charcoal for TeF_6, a second type of activated charcoal was evaluated briefly as a sorbent for TeF_6. The charcoal used for this study was activated cocoanut charcoal with a mono-layer capacity for TeF_6 of 7.43×10^{-3} mole/g. In this study, 2×10^{-3} mole of TeF_6 at approximately 200 Torr was reacted with a 10-g sample of cocoa-nut charcoal at 25°C. The results of the study showed that only 97% of the

TABLE V. Sorption Rate and Retention of Tellurium Hexafluoride on BPL Activated Charcoal at 25°C

TeF_6 charge, 2×10^{-3} mole; initial pressure, 200 Torr

Reaction Time (min)	Percent of Initial TeF_6 Sorbed on Activated Charcoal		
	1-g Sample[a]	5-g Sample[a]	10-g Sample[a]
0.5	69	98	>99
1.0	78	99	>99
2.0	86	>99	>99
5.0	93	>99	>99
10.0	94	>99	>99
15.0	95	>99	>99
20.0	95	>99	>99

Sorbent Sample Size (g)	Percent of Initial TeF_6 Desorbed from Charcoal during Evacuation[b]
1	36.5
5	1
10	1

[a] The calculated TeF_6 monolayer capacity of the BPL activated charcoal was 8.6×10^{-3} mole/g.

[b] The charcoal samples were placed under vacuum (~10^{-2} Torr) for desorption for $1\frac{1}{2}$ hr.

TABLE VI. Effect of Temperature on Sorption Rate and Retention of
Tellurium Hexafluoride on BPL Activated Charcoal

TeF$_6$ charge, 2 x 10^{-3} mole; initial pressure, 200 Torr;
charcoal charge,[a] 5 g

Reaction Time (min)	Percent of Initial TeF$_6$ Sorbed on Activated Charcoal Sample				
	25°C	100°C	200°C	300°C	400°C
0.5	98	98	27	4	0
1.0	99	>98	29	7	0
2.0	>99	>99	32	7	0
5.0	>99	>99	35	8	0
10.0	>99	>99	38	8	0
15.0	>99	>99	40	8	0
20.0	>99	>99	42	8	0

Temperature of Sorption and Desorption (°C)	Percent of Initial TeF$_6$ Desorbed from Charcoal during Evacuation[b]
25	1
100	3.7
200	35.7

[a] The calculated TeF$_6$ monolayer capacity of the BPL activated charcoal
was 8.6 x 10^{-3} mole/g.
[b] The charcoal samples were placed under vacuum (10^{-2} Torr) for desorp-
tion for about 1 hr.

tellurium hexafluoride present had been sorbed on a 10-g sample of cocoa-
nut charcoal in 20 min. When the sample was evacuated for 80 min at 25°C,
about 31% of the initial TeF$_6$ was desorbed. These results indicate that
cocoanut charcoal does not retain TeF$_6$ as well as BPL charcoal does.

3. Linde Molecular Sieves

a. Molecular Sieve 13X. The effect of TeF$_6$ surface loading
on the kinetics of TeF$_6$ sorption and TeF$_6$ retention by Molecular Sieve 13X
was investigated at 25°C. The results of this study, presented in Table VII,
indicate that TeF$_6$ is rapidly sorbed on Molecular Sieve 13X until 136% of
the B.E.T. surface area is covered by sorbed TeF$_6$. This high surface
coverage indicates that the tellurium hexafluoride molecule may be chemi-
cally reacting with the bulk material. Linde states the surface area of
Molecular Sieve 13X is about two to three times that determined by our
nitrogen B.E.T. surface-area measurements. Another series of sorption

studies (shown in Table VIII) was carried out to determine the effect of temperature on TeF_6 sorption on Molecular Sieve 13X, in both the presence and absence of a sodium fluoride trap at 100°C placed in series with the trap containing the sorbent. Sodium fluoride is commonly used to sorb hydrogen fluoride. Previous studies with sodium fluoride revealed that it does not react with TeF_6 at 100°C. The sorption studies at 300°C indicated that no significant amount of hydrogen fluoride, derived either from the TeF_6 feed or from interaction between TeF_6 and the sorbent, was present during the sorption step. The results of these studies indicate that Molecular Sieve 13X is a fairly good sorbent for TeF_6 below 200°C. Less than 4% of the TeF_6 was desorbed by evacuating the system to 10^{-2} Torr for 1 hr at temperatures up to 400°C.

TABLE VII. Sorption Rate and Retention of Tellurium Hexafluoride on Linde Molecular Sieve 13X at 25°C

TeF_6 charge, 2×10^{-3} mole; initial pressure, 200 Torr

Reaction Time (min)	Percent of Initial TeF_6 Sorbed on Molecular Sieve 13X		
	1-g Sample[a]	5-g Sample[a]	10-g Sample[a]
0.5	79	99	>99
1.0	84	>99	>99
2.0	91	>99	>99
5.0	>99	>99	>99
10.0	>99	>99	>99
15.0	>99	>99	>99
20.0	>99	>99	>99

Molecular Sieve 13X Sample Size (g)	Percent of Initial TeF_6 Desorbed from Molecular Sieve 13X during Evacuation[b]
1	36.5
5	1
10	1

[a]The calculated TeF_6 monolayer capacity of Molecular Sieve 13X was 1.16×10^{-3} mole/g.
[b]The Molecular Sieve 13X samples were placed under vacuum for desorption for 1 hr.

TABLE VIII. Effect of Temperature on Sorption Rate and Retention of Tellurium Hexafluoride on Linde Molecular Sieve 13X

TeF_6 charge, 2×10^{-3} mole; initial pressure, 200 Torr; Molecular Sieve 13X charge,[a] 5 g

Reaction Time (min)	Percent of Initial TeF_6 Sorbed on Molecular Sieve 13X				
	25°C	100°C	200°C	300°C[b]	400°C
0.5	99	>97	>91	76, 77	55
1.0	>99	>98	95	79, 79	62
2.0	>99	99	>98	84, 84	70
5.0	>99	>99	>99	92, 92	79
10.0	>99	>99	>99	95, 96	87
15.0	>99	>99	>99	96, 97	90
20.0	>99	>99	>99	96, 97	90

[a]The calculated TeF_6 monolayer capacity of Molecular Sieve 13X was 1.16×10^{-3} mole/g.
[b]The second of the two numbers represents the percent TeF_6 sorbed in the presence of a sodium fluoride trap for hydrogen fluoride.

Table IX presents nitrogen B.E.T. surface-area measurements on Molecular Sieve 13X before and after TeF_6 sorption at temperatures up to 400°C. No data are available, however, to indicate changes in surface area of Molecular Sieve 13X upon heating in the absence of TeF_6.

TABLE IX. B.E.T. Surface-area Measurements of
Linde Molecular Sieve 13X

Reaction time: 20 min

Description of Molecular Sieve 13X Sample	B.E.T. Surface Area (m^2/g)	Percent of Surface Covered with TeF_6
Material as received	280	-
Reacted at 100°C with TeF_6	24.3	34
Reacted at 200°C with TeF_6	25	34
Reacted at 300°C with TeF_6	8	34
Reacted at 400°C with TeF_6	13	31

b. Molecular Sieve 10X. Sorption studies of TeF_6 on Molecular Sieve 10X were performed by reacting 10- and 20-g samples of the sorbent at 25°C with 2×10^{-3} mole of TeF_6 at 200 Torr. The results of these studies showed that both the rate of TeF_6 sorption and the capacity of the Molecular Sieve for TeF_6 are comparable to those for Molecular Sieve 13X. However, the retention of TeF_6 by Molecular Sieve 10X was very poor.

4. Magnesium Fluoride, Sodium Fluoride, and Soda Lime

The sorption properties of 14-18 mesh MgF_2 for TeF_6 were evaluated at 25 and 200°C. At 25°C, the rate of TeF_6 sorption is rapid until about 10% of the surface is covered; at 200°C, the TeF_6 sorption rate is rapid until about 6.6% of the surface is covered. None of the TeF_6 sorbed by the MgF_2 was desorbed when the reaction product was evacuated to 10^{-2} Torr for 1 hr.

Sodium fluoride was evaluated as a sorbent for TeF_6 by reacting 2×10^{-3} moles of TeF_6 with 20-g samples of sodium fluoride at 100, 200 and 300°C. The results indicated no sorption.

Soda lime was evaluated by reacting 2×10^{-3} mole of TeF_6 with 20-g samples of soda lime at 25, 100, and 300°C. The results indicated that TeF_6 appears to sorb slowly on soda lime.

5. Chemical Traps

Kinetic studies were carried out on a group of reagents of low surface area which might react chemically with TeF_6 to form nonvolatile products. The

materials evaluated in this series of tests were copper turnings, nickel wool, copper(II) oxide, aluminum metal, and metallic tellurium powder.

Copper turnings were reacted with TeF_6 at 400 and 500°C. The results, shown in Table X, indicate that TeF_6 reacts rapidly with metallic copper at 500°C to form nonvolatile products. X-ray diffraction powder patterns showed Cu_2Te and CuF_2 to be the major reaction products. However, excessive air oxidation of the copper at 500°C eliminated this material from further consideration.

TABLE X. Reaction Rate of Tellurium Hexafluoride with Copper-metal Turnings and Nickel-metal Wool

TeF_6 charge, 2×10^{-3} mole; initial pressure, 200 Torr. Quantity of copper-metal turnings or nickel-metal wool charged to the system, 10 g.

Reaction Time (min)	Copper-metal Turnings		Nickel-metal Turnings	
	TeF_6 Reacted at 400°C (%)	TeF_6 Reacted at 500°C (%)	TeF_6 Reacted at 500°C (%)	TeF_6 Reacted at 500°C[a] (%)
0.5	74	98	11	1
1.0	82	99	16	4
2.0	89	>99	28	18
5.0	96	>99	78	80
10.0	97	>99	96	>98
15.0	97	>99	98	>98
20.0	97	>99	98	>98

[a]Nickel-metal wool prefluorinated with fluoride at 270°C.

Samples of nickel wool were reacted at 500°C with TeF_6. The nickel wool in one experiment was prefluorinated with fluorine at 270°C; it was not so treated in the other experiment. The data in Table X indicate that TeF_6 reacts slowly with nickel surfaces. X-ray diffraction patterns showed $NiTe$, $NiTe_2$, and NiF_2 to be reaction products.

Copper(II) oxide was essentially nonreactive at 400 and 500°C with TeF_6. Aluminum metal did not react with TeF_6 at temperatures up to 500°C. Only a slight reaction was noted between TeF_6 and tellurium metal powder at 370°C.

B. Gas-flow Sorption Studies

1. Activated Alumina--TeF_6-Air

Factorially designed experiments[10] were performed to determine the effects of four variables on the ability of activated alumina to remove TeF_6 from an air stream. The independent variables were

bed temperature, bed height, gas velocity, and TeF_6 gas concentration. Each variable was studied at two levels, as shown in Table XI. Since the effect of all the variables and an estimate of the first-order interactions could be obtained with a half-factorial design, the studies were restricted to half-factorial designs. (To study four variables completely and thus evaluate the effects and interactions, a factorial design consisting of 2^4 or 16 experiments would be required.) A half-replicate of eight experiments was carried out in this design with a ninth run for error evaluation. The results of these experiments were used to determine the effect of all the variables on the efficiency of TeF_6 removal by activated alumina and permitted an estimate of the first-order interactions. The design of the factorial experiments is presented in Table XII, where the variables are presented as (+) and (-) for the high and low levels, respectively.

TABLE XI. Levels of Variables Studied in Factorially
Designed Investigation with Activated Alumina

	Low Variable Level (-)	High Variable Level (+)
Bed temperature, °C	25	100
Bed height, in.	1	2
Gas velocity, ft/min	20	40
TeF_6 concentration, ppm	250	500

TABLE XII. Factorial Design of Experiments
with Activated Alumina

Sequence of Experiments	Level of Variables			
	Temperature	Gas Velocity	Bed Height	TeF_6 Concentration
1	-	-	+	+
2	-	+	-	+
3	+	+	+	+
4	+	-	-	+
5	-	+	+	-
6	-	-	-	-
7	+	-	+	-
8	+	+	-	-
9	-	-	+	+

Table XIII presents the experimental results for the sorption studies on activated alumina. A plot of the results of the experiments (Fig. 3) showed a linear relationship between the logarithm of the decontamination factor (DF) and the logarithm of the percent surface loading. From Fig. 3

TABLE XIII. Sorption of TeF$_6$ on Activated Alumina

Experiment Number	Background (cpm)	TeF$_6$ Loading[a] (%)	TeF$_6$ Activity Present on Bed No. 1[b] (cpm)	TeF$_6$ Activity Present on Bed No. 2[c] (cpm)	Observed DF[d]
1	89 ± 4	2.2	95,210	0 ± 6	>10,000
		5.2	221,450	20	11,070
		6.5	276,340	175	1,580
		9.9	422,780	5,390	78
		13.6	582,690	45,540	13
2	94 ± 4	3.8	76,710	5,770	13
		6.5	131,900	18,710	7
		8.8	176,680	35,830	5
3	107 ± 4	2.6	100,160	15.5	6,460
		5.15	202,600	1,130	180
		8.4	329,580	9,260	36
		10.0	394,210	21,730	18
4	94 ± 4	1.2	22,510	30	750
		2.2	40,620	110	369
		5.9	108,410	2,450	44
		8.6	158,470	8,200	19
		9.4	173,700	15,640	11
5	90 ± 4	2.1	71,960	60.5	1,190
		4.5	154,060	1,220	127
		6.65	229,190	6,110	38
		8.6	295,460	14,380	21
		10.5	360,620	25,960	14
6	90 ± 5	1.6	27,640	420	66
		3.66	61,600	3,200	19
		5.6	94,240	10,750	9
		8.0	134,990	26,570	5
7	96 ± 5	2.3	76,630	14	5,470
		4.8	160,150	600	266
		7.1	236,070	3,800	62
		8.44	281,100	8,590	33
8	96 ± 5	1.5	23,930	300	79
		3.2	52,440	2,245	23
		5.5	89,970	10,750	8
		7.7	126,750	20,480	6
9	105 ± 4	2.35	72,090	0 ± 6	>10,000
		5.80	177,480	61	2,910
		7.7	237,700	437	544
		10.1	310,360	2,390	130

[a]The percent TeF$_6$ surface loading is based on the B.E.T. surface area of the activated alumina, and assumes that at 100% TeF$_6$ loading, each sorbed TeF$_6$ molecule occupies 40 Å^2 of B.E.T. surface area.
[b]Bed No. 1 is the first of two beds placed in series for TeF$_6$ sorption.
[c]Bed No. 2 is the second of two beds placed in series for TeF$_6$ sorption.
[d]The observed DF is defined as the ratio of the TeF$_6$ concentration entering bed No. 1 to the TeF$_6$ concentration leaving bed No. 1.
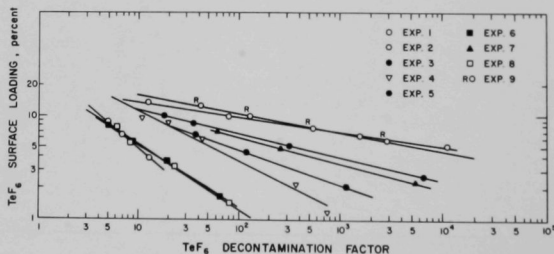
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Fig. 3. Decontamination of Air Streams from TeF$_6$ by Activated Alumina as a Function of TeF$_6$ Loading, Bed Temperature, Bed Height, Gas Velocity, and TeF$_6$ Concentration (see Table XII)

the magnitude of the effects of each variable on the efficiency of TeF_6 removal by activated alumina can be calculated at any loading or at any decontamination, the latter corresponding to the TeF_6 removal efficiency.

Two analyses on the effects of the variables were performed. In the first analysis, the effect of the variables on the log of the TeF_6 decontamination factor at 5% loading was determined; in the second analysis, the effect of the variables on the percent TeF_6 loading at 99.9% TeF_6 removal (DF = 1000) was evaluated. Table XIV shows the results of these analyses.

TABLE XIV. Effect of Variables in Factorially Designed Experiments with Activated Alumina

Increasing Variables	Effect[a] on TeF_6 Capacity at DF of 1000	Effect[b] on Log DF at 5% Loading
Temperature, 25-100°C	-0.22	-0.09
Gas velocity, 20-40 ft/min	-1.44	-0.68
Bed height, 1-2 in.	+3.71	+1.52
TeF_6 concentration, 250-500 ppm	+1.54	+0.74
Mean value of TeF_6 capacity and log DF, respectively	2.34	1.96
Interactions:		
(1) Gas flow-TeF_6 concentration or (2) Bed height-temperature	-0.79	-0.46
(1) Gas flow-bed height or (2) Temperature-TeF_6 concentration	-0.87	-0.31
(1) Bed height-TeF_6 concentration or (2) Temperature-gas flow	+1.16	+0.44
Standard deviation of effects	0.07	0.09

[a]Values expressed in percent loading.
[b]Values expressed in log DF.

Air purge studies to determine the stability of the sorbed TeF_6 on activated alumina indicated that the sorbed TeF_6 is stable toward dry air purges at flowrates of 20-40 ft/min for all TeF_6 loadings investigated. These air purges were of a 30-60-min duration.

The distribution of TeF_6 in the first or second sorbent bed for three experiments was determined; Table XV presents the results.

TABLE XV. Distribution of Tellurium Hexafluoride on Activated Alumina

Data from Bed No. 1 of Experiment 7

Position from Top of Bed[a] (in.)	Activity[b] of 1/4-in. Bed Sections at Particular TeF_6 Bed Loading[c] and DF			
	2.3%, DF = 5,470	4.8%, DF = 266	7.1%, DF = 62	8.44%, DF = 33
0 to 1/4	477	1,800	4,280	6,370
1/4 to 1/2	1,490	5,960	18,220	27,770
1/2 to 3/4	3,310	12,010	23,360	29,200
3/4 to 1	8,900	20,040	31,190	45,750
1 to 1-1/4	17,490	34,150	41,320	58,890
1-1/4 to 1-1/2	23,450	42,660	65,660	51,940
1-1/2 to 1-3/4	21,940	36,710	41,000	48,930
1-3/4 to 2	8,440	19,550	24,100	31,980

Data from Bed No. 1 of Experiment 8

Position from Top of Bed[a] (in.)	Activity[b] of 1/4-in. Bed Sections at Particular TeF_6 Bed Loading[c] and DF			
	1.5%, DF = 79	3.2%, DF = 23	5.5%, DF = 8	7.7%, DF = 6
0 to 1/4	5,190	11,380	19,350	28,260
1/4 to 1/2	6,190	17,520	31,070	40,500
1/2 to 3/4	6,870	14,070	25,290	30,290
3/4 to 1	5,350	9,320	16,540	19,210

Data from Bed No. 2 of Experiment 6

Position from Top of Bed[a] (in.)	Activity[b] of 1/4-in. Bed Sections at Particular TeF_6 Bed Loading[c] and DF			
	1.64%, DF = 66	3.7%, DF = 19	5.6%, DF = 9	8.0%, DF = 5
0 to 1/4	97	798	2,670	4,700
1/4 to 1/2	136	951	2,760	5,500
1/2 to 3/4	114	711	1,820	6,100
3/4 to 1	93	217	1,660	4,400

[a]Gas flow enters at bottom of the bed.
[b]The activity is expressed in cpm per 1/4-in. bed section.
[c]The TeF_6 bed loading is expressed in percent.

2. BPL Activated Charcoal--TeF_6-Air

A half-replicate factorial design of four experiments was carried out to determine the effects of bed height, gas velocity, and TeF_6 concentration on the ability of BPL activated charcoal to remove TeF_6 from a TeF_6-air mixture, with a fifth experiment for error evaluation. A complete factorial design for three variables is 2^3 or eight experiments. Table XVI presents the levels of the variables studied in these experiments. The design of the factorial experiments is presented in Table XVII, where the variables are presented as (+) and (-) for the high and low levels, respectively. Table XVIII and Fig. 4 present the results of the study

TABLE XVI. Levels of Variables Studied in Factorially
Designed Investigation with BPL Activated Charcoal

	Low Variable Level (-)	High Variable Level (+)
Bed height, in.	1	2
Gas velocity, ft/min	20	40
TeF$_6$ concentration, ppm	190	380

TABLE XVII. Factorial Design of Experiments
with BPL Activated Charcoal

Sequence of Experiments	Level of Variables		
	Gas Velocity	Bed Height	TeF$_6$ Concentration
1	+	+	-
2	+	-	+
3	-	-	-
4	-	+	+
5	-	-	-

TABLE XVIII. Sorption of TeF$_6$ on BPL Activated Charcoal

Experiment	Background (cpm)	TeF$_6$ Loading (%)	TeF$_6$ Activity Present on Bed No. 1[a] (cpm)	TeF$_6$ Activity Present on Bed No. 2[b] (cpm)	Observed DF[c]
1	165	2.4	154,700	-	-
		3.7	242,900	32	7,590
		4.4	288,400	190	1,520
		5.0	324,000	460	704
		5.6	364,300	1,230	296
2	100	2.0	64,130	117	548
		2.7	87,300	581	150
		3.4	108,300	1,450	75
		4.3	136,400	4,980	27
3	105	2.6	78,760	165	477
		3.3	102,000	580	176
		4.3	132,780	2,450	54
		5.1	157,400	5,250	30
4	105	4.4	265,000	6	44,160
		4.8	288,000	167	1,720
		5.0	298,600	300	995
5[d]	105	2.9	86,000	215	400
		3.7	109,000	1,400	78
		4.2	124,800	5,300	24

[a]Bed No. 1 is the first of two beds placed in series for TeF$_6$ sorption.
[b]Bed No. 2 is the second of two beds placed in series for TeF$_6$ sorption.
[c]The observed DF is defined as the ratio of the TeF$_6$ concentration entering bed No. 1 to the TeF$_6$ concentration leaving bed No. 1.
[d]Experiment 5 is a duplicate of Experiment 3 and was run to estimate the error.
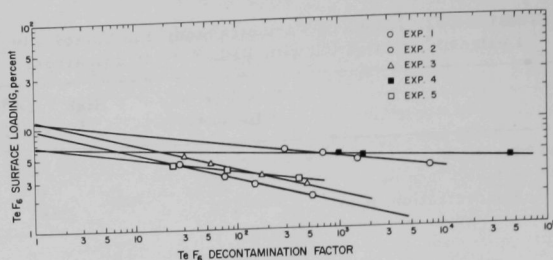
Fig. 4. Decontamination of Air Streams from TeF$_6$ as a Function of Bed Loading Using BPL Activated Charcoal

The results again showed a linear relationship between the logarithm of the DF and the logarithm of the percent TeF$_6$ loading. From Fig. 4 the magnitude of the effects of each variable can be calculated at any loading or at any decontamination, the latter corresponding to the TeF$_6$ removal efficiency. The effect of variables on the percent TeF$_6$ loading at 99.9% TeF$_6$ removal (DF = 1000) was evaluated. Table XIX presents the results of this analysis.

TABLE XIX. Effects of Variables in Factorially Designed Experiments with BPL Activated Charcoal

Increasing Variables	Effect on TeF$_6$ Capacity at DF of 1000[a]
Gas velocity, 20-40 ft/min	-0.33
Bed height, 1-2 in.	+2.90
TeF$_6$ concentration, 190-380 ppm	0.0
Mean value of TeF$_6$ capacity at DF = 1000	3.37
Standard deviation of effects	0.13

[a]Values expressed in percent loading.

3. Magnesium Fluoride--TeF$_6$-Air

Studies of magnesium fluoride as a sorbent for TeF$_6$ were performed in a single experiment at 25°C on a 2-in. sorbent bed at a gas velocity of 20 ft/min and a TeF$_6$ concentration of 500 ppm. The results of this study (presented in Table XX) indicate that magnesium fluoride is a poor sorbent for TeF$_6$.

TABLE XX. Sorption of TeF$_6$ on Magnesium Fluoride in a Gas-flow System

Background (cpm)	TeF$_6$ Loading (%)	TeF$_6$ Activity Present on Bed No. 1 (cpm)	TeF$_6$ Activity Present on Bed No. 2 (cpm)	Observed DF
107	1.53	10,752	5,697	1.9
	2.52	17,768	9,257	1.9

4. Linde Molecular Sieve 13X--TeF$_6$-Air

Batch TeF$_6$ sorption studies on Molecular Sieve 13X indicated that this material possesses fairly good sorptive properties toward TeF$_6$. Gas-flow sorptive studies, however, performed under conditions that were near optimum for sorption of TeF$_6$ on other sorbents (Experiments 1 and 2, Table XXI), indicate that Molecular Sieve 13X possesses only fair TeF$_6$ sorptive properties. The results also show a linear relationship between the logarithm of the calculated DF and the logarithm of the percent TeF$_6$ loading.

TABLE XXI. Sorption of TeF$_6$ by Linde Molecular Sieve 13X and by Activated Alumina from a Gas-flow System[a]

Experiment	Background (cpm)	TeF$_6$ Loading (%)	TeF$_6$ Activity Present on Bed No. 1 (cpm)	TeF$_6$ Activity Present on Bed No. 2 (cpm)	Observed DF
1	109	1.2	28,453	125	228
		4.0	95,596	2,110	45
		6.3	150,492	7,308	20
		9.0	213,270	19,048	11
2	102	1.60	37,618	42	896
		3.35	78,930	308	256
		6.37	150,053	2,001	75
3[b]	89	2.2	95,213	0	>10,000
		5.2	221,454	20	11,070
		6.5	276,342	175	1,580
		9.9	422,780	5,392	78

[a]Experiments 1 and 2 were carried out at 25°C on a 2-in. bed of Molecular Sieve 13X at a TeF$_6$ concentration of 500 ppm. In Experiment 1, the gas velocity was 40 ft/min; in Experiment 2, it was 20 ft/min.
[b]Activated alumina-TeF$_6$ study under variable conditions comparable to Experiment 2 (see Experiment 1, Table XIII).

5. Activated Alumina--TeF$_6$-F$_2$-Air

The presence of fluorine in fluoride-volatility process off-gas streams fed to the TeF$_6$ sorption trap must be considered. Upstream from the TeF$_6$ sorption trap, the off-gas will be passed through a fluidized bed of activated alumina, where nearly all the fluorine will be removed without the bed caking observed when a high concentration of fluorine is passed through a packed bed of activated alumina. Nevertheless, low concentrations of fluorine will be present in the gas stream fed to the TeF$_6$ sorption trap. The potential hazard of an uncontrolled charcoal-fluorine reaction

makes the use of BPL charcoal less desirable than alumina. Consequently, only a packed bed of activated alumina was evaluated for the removal of TeF_6 from a TeF_6-F_2-air stream.

The experiment was performed under conditions that gave the best TeF_6 decontamination in the earlier series of experiments with activated alumina--TeF_6-air, that is, at 25°C, a TeF_6 concentration of 500 ppm, a 2-in. bed of activated alumina, and a gas velocity of 20 ft/min. The fluorine concentration was arbitrarily set at 500 ppm. The results of this study are presented as Experiment 1 in Table XXII and Fig. 5, along with the results obtained for activated alumina under experimental conditions comparable to the conditions used in Experiment 1, but in a fluorine-free system (see Experiment 1, Table XII). Figure 6 shows the TeF_6 profile at various bed loadings of bed No. 1 in Experiment 1.

TABLE XXII. Sorption of TeF_6 by Activated Alumina from a
Gas-flow System with and without Elemental Fluorine

Experiment	Background (cpm)	TeF_6 Loading (%)	TeF_6 Activity Present on Bed No. 1 (cpm)	TeF_6 Activity Present on Bed No. 2 (cpm)	Observed DF
1	121	1.05	10,500	0 ± 5	1,000
		4.82	48,050	28	1,714
		7.03	70,000	203	345
		8.84	88,000	647	136
		11.76	117,150	3,000	39
2[a]	89	2.2	95,213	0 ± 5	10,000
		5.2	221,454	20	11,070
		6.5	276,342	175	1,580
		9.9	422,780	5,392	77

[a]Activated alumina-TeF_6 study under variable conditions that are comparable to conditions for Experiment 1, but in a fluorine-free system (see Experiment 1, Table XII).
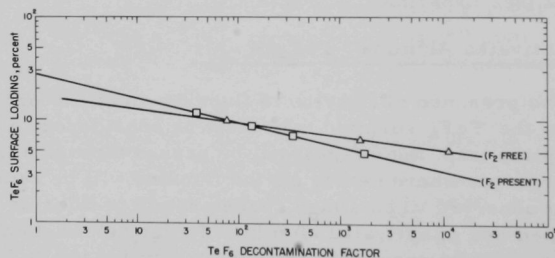

Fig. 5. Decontamination of Air-Fluorine Streams from TeF_6 by
Activated Alumina as a Function of Bed Loading
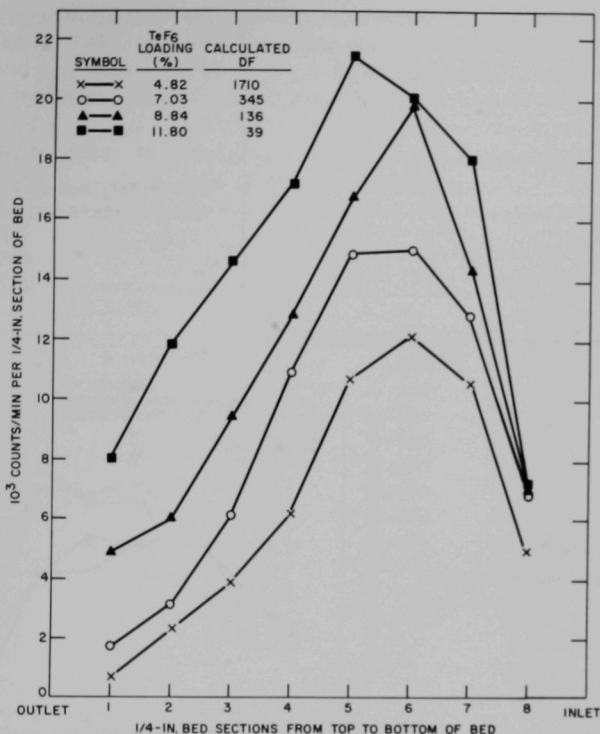
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Fig. 6. Profile of TeF$_6$ Sorbed on Activated Alumina
in the Presence of Fluorine

The presence of fluorine in the TeF$_6$-containing gas stream may also cause displacement of previously sorbed TeF$_6$ from activated alumina. To evaluate the importance of this potential problem, a 2-in. bed of activated alumina was surface-loaded with approximately 13.8% radio-tagged TeF$_6$ under the experimental conditions used in Experiment 1 (Table XII). At this point, the DF across the bed was 12.8. Bed No. 2, the second bed in series, was replaced with a fresh 2-in. bed of activated alumina. An air-fluorine gas mixture at a flowrate of 20 ft/min and a fluorine concentration of 1000 ppm was then passed into bed No. 1, and the gases exiting from the top of bed No. 1 were adjusted to a tellurium hexafluoride concentration of 500 ppm with nonradioactive TeF$_6$. The removal of TeF$_6$ from bed No. 1 was accompanied by the buildup of activity on bed No. 2 and by changes in the TeF$_6$ profile on bed No. 1, both as a function of time. Figure 7 shows the buildup of activity on bed No. 2; Fig. 8 shows the profile of TeF$_6$ on bed No. 1 as a function of the fluorination time. These studies clearly indicate that fluorine does displace tellurium hexafluoride from activated alumina.
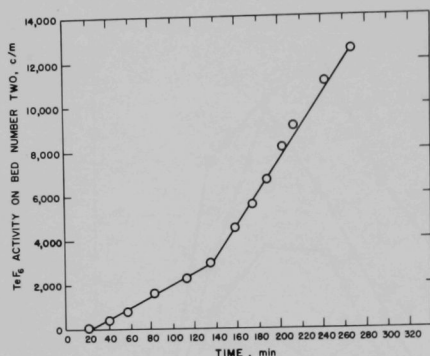
Fig. 7

Rate of TeF$_6$ Buildup on Bed No. 2
during Fluorination of Bed No. 1

308-1086

Fig. 8

Profile of TeF$_6$ on Activated Alumina
as a Function of Fluorination Time
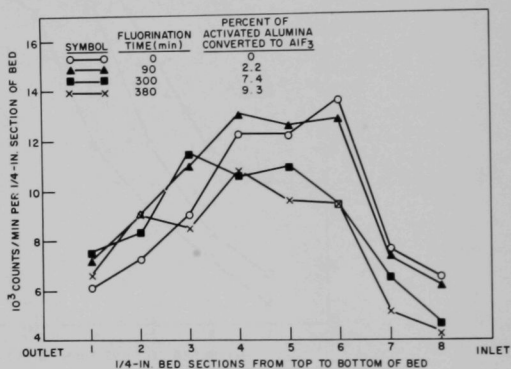
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The results of Experiment 1 (Table XXII) were extrapolated in
Fig. 5 to give a value of 28% TeF$_6$ surface loading at DF = 1. This means
that the maximum obtainable TeF$_6$ surface loading on activated alumina
under the experimental conditions studied is 28%. To verify this maximum
surface loading and to better understand how bed depth affects the removal
efficiency of TeF$_6$ and its retention during subsequent fluorination with
elemental fluorine, studies were performed on 6-in. packed beds of acti-
vated alumina. Tellurium hexafluoride loading profiles for the activated
alumina beds were obtained during the TeF$_6$ loading step and during the
subsequent bed-fluorination step. The TeF$_6$ sorption step in this study
was carried out under the same experimental conditions as those in
Experiment 1, Table XXII, except for the bed length.

The results of the sorption study are presented in Table XXIII
and show that maximum TeF$_6$ surface loadings in excess of 25% are ob-
tained on the lower 2 in. of the 6-in. bed, and that 17 and 1% surface load-
ings are obtained for the middle and top 2-in. bed sections, respectively.
Examination of the individual 1/4-in. bed sections reveals bed loadings in

excess of 33% in the lower bed sections and 0% loadings in the upper bed sections. These TeF_6 surface-loading results confirm the extrapolated maximum average value of 28% TeF_6 surface loading. The overall DF for the 6-in. bed was >20,000 at the maximum loading level studied.

TABLE XXIII. Distribution of Tellurium Hexafluoride on a
6-in. Bed of Activated Alumina

Bed Sections (1/4-in.) from Bottom to Top of Bed	Activity[a] (in cpm) of 1/4-in. Bed Sections When Lower 2 in. of Bed Had Bed-loading Percentages Stated				
	6.3%	12.4%	21%	25%	25.5%
1	3,540	6,000	6,640	7,000	7,800
2	6,360	8,200	12,800	13,200	11,200
3	6,970	13,600	16,200	17,600	20,600
4	7,150	12,600	18,800	21,400	21,400
5	3,830	8,200	16,200	17,200	18,000
6	2,750	8,200	14,600	21,000	22,000
7	1,830	4,600	13,600	16,600	18,000
8	_b	2,100	10,800	18,600	15,400
9		232	4,400	12,000	15,200
10		110	2,400	9,200	15,000
11		_b	1,600	8,400	15,000
12			800	5,000	13,800
13			_b	5,800	12,000
14				1,000	9,400
15				_b	7,000
16					4,600
17					2,800
18					1,600
19					500
20					_b
21					
22					
23					
24 (Top 1/4-in. section of 6-in. bed)					

[a]An activity of 5,270 cpm per 2 in. of bed is equal to 1% TeF_6 surface loading.
[b]Level of activity was equal to background.

This 6-in. bed of activated alumina, loaded with TeF_6, was next fluorinated with fluorine at a concentration of 12,200 ppm and at a gas velocity of 20 ft/min. The results of this study (shown in Table XXIV) indicated that fluorine partially displaces the sorbed TeF_6 from the activated alumina surface. The initial removal of the TeF_6 from the 6-in. bed was noted after 0.022 mole of fluorine had passed into the bed. During the period when 0.1 mole of fluorine was injected into the bed, 5% of the TeF_6 present

was removed from the bed; during the period when 0.2 mole of fluorine was injected, 9% of the TeF_6 was removed from the bed. Table XXIV shows the profile of the TeF_6 on the bed as a function of the fluorine injected.

TABLE XXIV. TeF_6 Profile on a 6-in. Bed of Activated Alumina after Fluorine Injections of 0.1 and 0.2 mole

Bed Sections (1/4-in.) from Bottom to Top of Bed	Activity (in cpm) of 1/4-in. Bed Sections after Stated Fluorine Injections		
	0 mole of F_2	0.1 mole of F_2	0.2 mole of F_2
1	7,800	3,000	3,400
2	11,200	7,600	4,400
3	20,600	9,600	6,200
4	21,400	8,400	11,000
5	18,000	13,000	12,400
6	22,000	13,000	12,600
7	18,000	13,600	10,600
8	15,400	11,400	12,200
9	15,200	15,000	14,400
10	15,000	13,400	12,600
11	15,000	13,600	12,200
12	13,800	10,200	10,800
13	12,000	13,000	12,000
14	9,400	11,600	11,600
15	7,000	9,400	11,000
16	4,600	11,400	11,000
17	2,800	9,600	8,600
18	1,600	7,400	8,000
19	500	8,800	8,000
20		5,800	6,400
21		5,000	4,600
22		3,600	3,600
23		1,800	1,800
24		1,200	1,200
Total cpm	231,300	220,400	210,600
Percent TeF_6 Removed by Fluorine	0.0	5	9

The first 6-in. bed warmed slightly (~50°C) during the fluorination step, but became cool again after 0.080 mole of fluorine had passed into it. Bed No. 2 then became warm until about 0.179 mole of fluorine had been injected into the system.

Since a 6-in. bed of activated alumina has a surface capacity for fluorine of 0.074 mole (if one assumes that a sorbed fluoride ion occupies 10 $\mathring{A}^2$ of B.E.T. surface area or the approximate area occupied by a F^- on the face of crystalline aluminum fluoride), only the surface of the activated alumina is apparently being converted to fluoride during the

fluorination step in these experiments. Conversion to AlF_3 of 30 g of activated alumina (6-in. bed) requires about 1 mole of fluorine, if one assumes the following reaction:

$$Al_2O_3 \cdot H_2O + 4F_2 \rightarrow 2AlF_3 + 2HF + 2O_2.$$
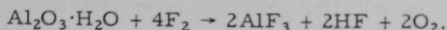
To determine whether activated alumina that has been fluorinated is an effective sorbent for TeF_6, the following study was made. Packed beds of activated alumina, 2 in. high, were charged to the gas-flow apparatus. The beds were then contacted with approximately 0.2 mole of fluorine. Surface-area measurements on the fluorinated activated alumina gave a nitrogen B.E.T. surface area of 125 m^2/g. Sorption studies with TeF_6 were then carried out with the beds, using the experimental conditions employed in Experiment 1, Table XXII. The conditions were: (1) gas velocity, 20 ft/min, (2) bed height, 2 in., (3) temperature, 25°C, (4) TeF_6 concentration, 500 ppm, and (5) fluorine concentration, 500 ppm. The study was repeated with no fluorine in the gas mixture. In both cases, no TeF_6 was sorbed. The results of these studies indicate that fluorinated activated alumina has little or no capacity for tellurium hexafluoride.

C. Heat-of-sorption Studies on Activated Alumina-TeF$_6$

A series of TeF_6 sorption studies was performed on activated alumina to obtain sorption isotherms from which the heat of sorption could be estimated. The isotherms were obtained at 5, 26, 40, and 60°C and are presented in Fig. 9. From a plot of the pressure of TeF_6 above the alumina against the reciprocal absolute temperature for the percent surface loadings of sorbed TeF_6, the heat of sorption can be determined by using the equation
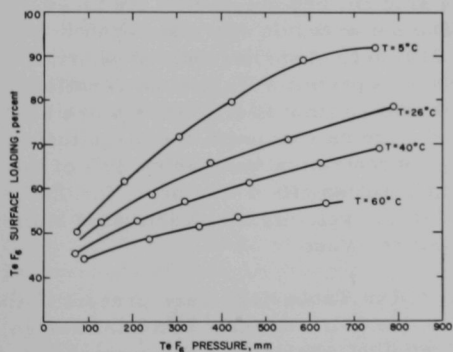
$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.3R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right),$$

Fig. 9. Sorption Isotherms for TeF$_6$ on Activated Alumina

where ΔH is the heat of sorption in cal/mole, R is a constant, and P_1, P_2, T_1, and T_2 are the pressures and absolute temperatures. From such a plot, ΔH was found to be 5 kcal mole^{-1}. In comparison, the heat of sublimation[5] for TeF_6 is 6 kcal mole^{-1}. The value of 5 kcal for the heat of sorption is a typical value for physical adsorption on a solid sorbent.

IV. DISCUSSION

The results of the batch-type sorption studies revealed that of the sorbents studied, activated alumina, BPL activated charcoal, Linde Molecular Sieve 13X, magnesium fluoride, and copper-metal turnings showed the greatest ability to rapidly sorb and retain TeF_6. The fact that copper-metal turnings would probably corrode to the oxide fairly rapidly at 500°C in an air system removed this material from further consideration. The magnesium fluoride, although not appearing to possess a high capacity for TeF_6, did exhibit excellent retention of TeF_6, and further studies seemed warranted. The activated alumina seemed the most promising of the reagents since it appeared to be effective over a wide temperature range; it is relatively inexpensive and has been used in fluid-bed fluoride-volatility process systems for off-gas treatment. BPL activated charcoal and Linde Molecular Sieve 13X also appeared promising as sorbents for TeF_6.

The preliminary batch-type screening studies also indicated that the TeF_6 was probably sorbed on the surface of the sorbents. The sorption isotherms for TeF_6 on activated alumina indicate a heat of sorption of 5 kcal mole^{-1} (see Fig. 9) and possess many of the characteristics typical of surface sorption isotherms. Thus, surface sorption was assumed in the simple treatment of sorption data in this report.

The results obtained from the half-factorial design with activated alumina revealed that of the variables studied, bed height was the most important in the gas-flow systems. The same result was also found in the factorially designed experiment with BPL activated charcoal. A short, 1-in. bed (see Table XV) does not appear to permit a TeF_6 concentration gradient to develop. Consequently, low TeF_6 removal efficiencies are obtained in shallow beds. When activated alumina was used, the magnitudes of the effects of gas velocity and TeF_6 concentration were about 40% of the effect of bed height; when charcoal was used, no effect was noted for TeF_6 concentration and only a slight effect for gas velocity. With activated alumina sorbent, there was little or no temperature effect.

Interactions of variables (as listed in Table XIV) were present in the study with activated alumina. However, the half-replicate factorial design does not permit (over the small range studied) the proper assignment for these interactions.

The DF's obtainable for TeF_6 on packed beds of activated alumina or BPL activated charcoal exceed the calculated DF required for TeF_6 (1350) for a fluoride-volatility process.

Cursory studies of magnesium fluoride indicate this material to be unsatisfactory as a sorbent for TeF_6. The magnesium fluoride appears to react as a whole with the TeF_6 and not just on its surface since the DF did

not change with apparent surface loading. Gas-flow sorption studies on
Molecular Sieve 13X clearly indicate that DF's in excess of 1000 could not
be obtained under the conditions studied. The poor sorption-rate properties
of the Molecular Sieve 13X probably are related to the uniformity of its
pores, which are approximately 10-13 Å in diameter and apparently are
filled during TeF_6 sorption (see B.E.T. surface-area measurements,
Table IX). Similar studies on activated alumina indicated that sorbed TeF_6
had no effect on its B.E.T. surface area.

Activated alumina, currently being used at ANL to remove fluorine
from gas streams, was investigated as a packed-bed sorbent for TeF_6 in
streams that contain fluorine. Since TeF_6 sorption studies using high
fluorine concentrations and corresponding high bed temperatures cannot
be easily performed in the laboratory, cursory studies were made to deter-
mine whether suitable TeF_6 DF's could be obtained in the presence of fluo-
rine at low levels and whether fluorine would displace the TeF_6 once TeF_6
was sorbed on a bed of activated alumina. The results of these studies
(plotted in Fig. 5) indicate that the presence of fluorine has a slight effect
on the TeF_6 DF at levels of 500 ppm. Fluorine, however, does have the
ability to displace the sorbed TeF_6 (as may be seen from Figs. 7 and 8).
Consequently, precautions should be taken to ensure that the beds of acti-
vated alumina are sufficiently deep to prevent fluorine from displacing the
TeF_6 in the bed. The maximum TeF_6 surface loading of 25% obtained on
a 6-in. bed of activated alumina in the presence of fluorine (as noted in
Table XXIII) is quite significant. This result not only confirms the relation-
ship between the removal efficiency of a bed and the amount of material
already sorbed on the bed, but also reveals that, under the experimental
conditions studied, a 6-in. bed is capable of removing >99.99% of TeF_6 while
developing a TeF_6 loading of 25% on the lower 2 in. of the bed.

The results of these studies indicate that packed beds of activated
alumina are capable of properly decontaminating the fluid-bed fluoride-
volatility process off-gas stream for TeF_6 in the presence of low levels of
fluorine. If fluid beds of activated alumina are placed upstream from the
packed beds of activated alumina, good TeF_6 decontamination at any level of
fluorine in the off-gas system should be achieved.

APPENDIX A

Nuclear Technology and Tellurium Hexafluoride

The fluorination of fission-product tellurium by the various fluorinating agents has been assumed by most workers to result in the formation of the volatile tellurium hexafluoride. Campbell and Robinson[11] showed that at high temperatures (>150°C), the only reaction product formed between tellurium and fluorine is tellurium hexafluoride. Since the proposed three-step fluoride-volatility process will involve contacting the fission-product tellurium with both BrF_5 and fluorine at temperatures above 300°C, the fission-product tellurium that enters the off-gas system is assumed to be tellurium hexafluoride. A literature review on the subject[5] revealed that no quantitative information was available on the removal of tellurium hexafluoride from off-gas generated in fluoride-volatility processes. Chilenskas,[12] as well as French workers,[13] found that activated at 450-650°C alumina is effective in removing tellurium hexafluoride from process off-gases. Charcoal traps, when used in series with activated alumina, are effective in removing small amounts of tellurium hexafluoride.[12] Studies by Krause and Potts[14] showed that sodium fluoride does not sorb tellurium hexafluoride in the range of 100-300°C.

Studies at ORNL[15] indicated that an absorption system consisting of a packed column of Alundum saddles, through which a 10% aqueous solution of potassium hydroxide is circulated at 50-70°C, is relatively effective in hydrolyzing tellurium hexafluoride. Attempts to obtain quantitative results in these hydrolysis studies were unsuccessful. The caustic-spray absorption system used for fluorine disposal in the Oak Ridge Volatility Pilot Plant is capable of removing some of the tellurium, but not enough to ensure that none accompanies the residual effluent.[16] Tellurium hexafluoride also reacted with nickel at temperatures near 300°C. Laboratory tests of the ability of packed beds of nickel mesh, in 1-in.-diam nickel tubes, to remove tellurium hexafluoride were performed and are summarized in Table XXV.

TABLE XXV. Retention of Tellurium in Beds of Nickel Mesh at 400-600°C[16]

Conditions: Mixtures of 15-25% TeF_6[a] passed through beds of nickel mesh (1 in. in diameter and 6 in. long) at 100 ml (STP)/min for 0.5 hr

| Temp (°C)[b] | Tellurium Retained (%) | | | | | | Reactor Wall[c] | Aqueous KOH Trap | Material Balance (%) |
| | Bed Section (in order of use) | | | | | | | | |
	1	2	3	4	5	6			
400	61.8	24.8	1.9	0	0	0			88.5
500	17.7	11.6	4.7	7.2	13.4	10.0	8.7		73.3
600	8.7	4.4	4.7	3.8	0	0	41.4		63.0
400	0	24.5	38.5	1.8	0.2	0		0.7	65.7
450	20.7	44.7	1.4	0	0	0		0	66.8
480	43.6	13.0	1.0	0.7	0	0		0	58.3

[a]Balance of feed gas is helium.
[b]Temperatures in the last three runs were believed more accurate than others because of improvements in thermocouples.
[c]Determined by total dissolution.

Tellurium retention in the hot nickel bed is probably by the formation of nickel tellurides, nickel fluoride, and metallic tellurium, not the formation of Te_2F_{10} and TeF_4 as reported. Gunther and Steindler[17] found that when tellurium hexafluoride and metallic nickel coupons are reacted at 500°C for 18.9 hr, nickel tellurides ($NiTe$, $NiTe_2$) and nickel fluoride are formed. The reaction products were isolated from the corroded nickel coupons and identified by X-ray diffraction. Metallic tellurium was also found on the nickel wire used to suspend the nickel, Monel, and Inconel coupons. High-temperature caustic-spray towers have been considered at ORNL for the removal of tellurium hexafluoride from off-gas streams.[18]

APPENDIX B

Calculation of the Required Decontamination Factor for Tellurium in Fluid-bed Fluoride-volatility Process (FBFVP)

Since little information is available on the future fluoride-volatility plant processes, certain assumptions had to be made about the process in order to estimate what fraction of the tellurium in the off-gas stream of a FBFVP must be removed. The following assumptions were made:

1.   The proposed process was assumed to be a three-step oxidation-fluorination process, which consisted of (1) oxidation of the UO_2 fuel to U_3O_8 with oxygen, (2) fluorination of the U_3O_8 with BrF_5, and (3) fluorination of the residual plutonium with fluorine.

2.   The proposed fluoride-volatility plant would process one ton of oxide fuel per day.

3.   The feed gas was assumed to be 20 v/o BrF_5 and the balance nitrogen.

4.   No recycle of process gas was assumed.

5.   A 50% utilization of the BrF_5 in the fluorination step was assumed.

6.   The oxidation and fluorination of the UO_2 fuel were assumed to be described by the following equations:

$$3UO_2(s) + O_2(g) \rightarrow U_3O_8(s);$$

$$5U_3O_8(s) + 18BrF_5(g) \rightarrow 15UF_6(g) + 9Br_2(g) + 20O_2(g).$$

7.   The BrF_5 fluorination and release of the tellurium were assumed to be completed in 1, 3, or 6 hr. These different release times were selected to cover short, rapid releases of tellurium hexafluoride, as well as to show how the release rates affect the tellurium decontamination factor (DF).

8.   The reactor fuel was assumed to be BWR type with a 10,000-MWd/ton burnup. Higher burnups would only slightly alter the required tellurium decontamination factor, but would result in a greater concentration of TeF_6 in the off-gas.

9.   The Maximum Permissible Stack Discharge Rate (MPSDR) of the tellurium hexafluoride was calculated to be 10^{-2} Ci/sec; this value assumes a stack-gas dilution factor of 10^6 m^3/sec between the stack outlet and the ground.

10. The specific activity of the tellurium was assumed to be 0.35 Ci/mg of tellurium.[16]

11. The BrF_5 fluorination of the U_3O_8 was assumed to require 12 hr.

One ton of BWR (boiling-water reactor) fuel with a 10,000-MWd/ton burnup contains 4.82×10^4 Ci or 147 g of tellurium.[19] The amount of tellurium in the off-gases with no tellurium removal by decontamination would thus vary from 13.39 to 4.46 to 2.23 Ci/sec for 1-, 3-, and 6-hr release times, respectively. Since the MPSDR for tellurium was estimated at 10^{-2} Ci/sec, the decontamination factors required are 1339, 446, and 223, respectively. These decontaminations are equivalent to 99.925, 99.775, and 99.55% removal, respectively. These decontamination factors are based on a MPC_{168} (maximum permissible concentration for continuous exposure) of 10^{-8} Ci/m^3.[3]

Knowledge of the decontamination factors required for tellurium is not sufficient to describe the system since the required decontamination factors must be attained by using off-gas containing the expected concentrations of tellurium. In the calculation of these concentrations of tellurium at the MPSDR, a BWR-type fuel was selected. The assumptions made in this calculation have in part been presented earlier in this report; other assumptions are presented in the following calculations: One ton of UO_2 fuel is equivalent to 3.356×10^3 moles of UO_2, which on oxidation yields 1.119×10^3 moles of U_3O_8. The U_3O_8 in turn releases 4.48×10^3 moles of oxygen when fluorinated. The fluorination of the U_3O_8 requires 8.06×10^3 moles of BrF_5, since only 50% of the BrF_5 is utilized. This means that 3.22×10^4 moles of nitrogen are required, or 3.67×10^4 moles of nonfission-product off-gas is passed through the system in the 12-hr BrF_5 fluorination of the U_3O_8. It is assumed in this calculation that the reaction products containing bromine and the unreacted BrF_5 will be cold-trapped from the off-gases. The 3.67×10^4 moles of off-gases released during a 12-hr period are equivalent to 8.23×10^5 liters of gas (STP). The off-gas release rate will thus be 19 liters/sec. Since the estimated MPSDR for tellurium is 10^{-2} Ci/sec or 5.36×10^{-3} ml of tellurium hexafluoride per second, the concentration of tellurium hexafluoride in the off-gases at the estimated MPSDR should be no greater than 0.28 ppm by volume. Table XXVI presents calculated tellurium hexafluoride gas concentrations and DF requirements for off-gas handling at various TeF_6 release periods.

TABLE XXVI. Calculated Tellurium Hexafluoride Concentrations and Decontamination-factor Requirements for Off-gas from a Fluid-bed Fluoride-volatility Process

Percent BrF_5	Percent N_2	TeF_6 (ppm) in Off-gas for Indicated TeF_6 Release Periods[a]			DF Required[b]		
		1 hr	3 hr	6 hr	1 hr	3 hr	6 hr
20	80	375	125	63	1339	446	223
100	–	3072	1024	512	1339	446	223

[a]TeF_6 (in ppm by volume) in the off-gas to the off-gas handling system for the indicated gas release periods.
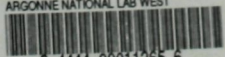[b]DF required to meet MPC requirements (see text) for indicated TeF_6 release periods.

ACKNOWLEDGMENTS

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